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PHYSICAL CHEMISTRY

1965

SovietRxiv

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Abstract

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UDC 541.64.145

PHYSICAL CHEMISTRY

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STUDY OF THE STRUCTURE OF SOLUTIONS OF CRYSTALLIZING POLYMERS

Quite recently ([1,2]), with the aid of new electron-microscopic methods for direct observation of the structure of polymers in solutions, it was shown that in solutions, at certain concentrations, supramolecular structures arise which are very similar to the structures observed in solid amorphous polymers. This morphological similarity indicates that the formation of nuclei of a polymer body already takes place in solution.

Fig. 1. Schematic diagram of the setup:
I –light source; C –stabilizer; K –condenser; D –diaphragm; L_1, L_2, L_3 –lenses; Sh –slit; P –polarizer; A –analyzer; T_1, T_2 –thermostats; F –photomultiplier; PS –self-recording potentiometer

On the basis of these results it could be assumed that the presence of supramolecular structures in solutions of crystallizing polymers must in a definite way affect the kinetics of crystallization of polymers from solutions. Such an assumption is based on the fact that the stable associates formed in solution apparently should facilitate the process of nucleation. In this case the induction period of crystallization, the magnitude of which depends to a substantial degree on whether homogeneous or heterogeneous nucleation of a new phase takes place, can serve as a reliable criterion of the structuring of the solution.

These considerations formed the basis of the proposed method. By studying the kinetics of crystallization from solutions, or, more precisely, the dependence of the induction period on the previous history of the solution (temperature and duration of heating), one can obtain an idea of the nature and character of the order of crystallizing polymers in their solutions.

To study the kinetics of crystallization from solution, a method was used based on the principle of depolarization of light by crystals, which is successfully applied to the study of the kinetics of crystallization of polymers from melts ([3]).

Fig. 2. Sketch of the cuvette

Figure 2: Fig. 2. Sketch of the cuvette

The essence of the method is as follows. The solution under study is placed in a field of crossed nicols. As the crystallization process proceeds, depolarization of the light occurs. Recording the rate of change in the intensity of the transmitted light makes it possible to study the kinetics of this process. The schematic diagram of the setup is shown in Fig. 1. Polaroids were used as the polarizer and analyzer; their advantage over Nicol prisms consists in the absence of limitations associated with a fixed aperture angle and in the possibility of obtaining a polarized light beam of the required diameter. The polarized light beam passes through a liquid thermostat, into which a cuvette containing the solution under study is placed. A sketch of the quartz cuvette is shown in Fig. 2. The small volume of the cuvette (1.5–2.0 ml) and its relatively large surface area ensured the rapid attainment of isothermal conditions.

The time for thermostating with a temperature drop of 50° (from 130 to 80°), calculated theoretically and determined experimentally by means of a thermocouple, was about one minute.

The object of the investigation was fractionated (4) linear polyethylene with a molecular weight of 50,000. Decalin was used as the solvent. The equilibrium dissolution temperature, estimated by the balance-weighing method, was 100 –105°. The choice of a high-boiling solvent (b.p. 190–195°) made it possible to study the thermal prehistory of the sample at 50–60° above the equilibrium dissolution temperature.

Fig. 2. Sketch of the cuvette

The solutions studied, with a concentration of 0.15%, were prepared as follows. Polyethylene with a stabilizer was dissolved in distilled decalin at 150° for one and a half hours. After the cuvette was filled with the solution and cooled, the resulting suspension was held for a definite time at the desired temperature in a glycerin thermostat above the equilibrium dissolution temperature and then was rapidly transferred to a water thermostat, where crystallization was carried out.

From the isotherms obtained, the induction period was determined as the interval of time during which no depolarization of light is observed, i.e., the intensity of the transmitted light remains constant. It should be noted that the isotherms obtained by means of the method used can be successfully employed for studying the overall kinetics of crystallization of polymers from dilute solutions. However, in the present work, mainly the results of studying the induction periods of crystallization will be presented, since they make it possible to draw certain conclusions about the structure of crystallizing solutions.

Fig. 3.

Fig. 3.

Figure 3: Fig. 3.

To solve this problem, it was first necessary to choose the optimal experimental conditions—the crystallization temperature and the duration of heating above the equilibrium dissolution temperature. The crystallization temperature had to be characterized by an induction period known to be longer than the time required to attain isothermal conditions, while the working isotherm had to have a sufficiently distinct form—especially its initial portion (Fig. 3).

For this purpose the dependence of the induction period on the crystallization temperature at a fixed dissolution temperature was investigated. As is seen from Fig. 4, the optimal crystallization temperature is 78°, since the induction period lies within 6–7 min. (the thermostating time is of the order of 1 min.), and the beginning of crystallization is clearly visible.

To exclude the influence of heterogeneous nuclei, which may be particles of incompletely dissolved polymer, the dependence of the induction period on the duration of heating of the sample at constant dissolution and crystallization temperatures was studied. The curve in Fig. 4 shows that, with increasing heating duration, the induction period increases, reaching a definite value for a fixed dissolution temperature. It turned out that, over the entire temperature interval investigated, a heating time of about 60 min. is quite sufficient to exclude nonequilibrium factors associated with incomplete melting and dissolution of the substance.

Figure 4 presents the dependence of the induction period on the dissolution temperature. As is seen from the graph, as the equilibrium dissolution temperature (100–105°) is approached, the induction period

decreases, and it changes nonmonotonically. Above 125°, the induction period does not depend on the dissolution temperature and is of the order of 6 min. At temperatures below 120°, the induction period decreases to a value of the order of 4 min 25 sec. The most noteworthy fact is the sharp change in the magnitude of the induction period within a narrow temperature interval (5°).

The experimental results obtained indicate that above 120–125° we have a transition from heterogeneous to homogeneous nucleation. It is quite natural to suppose that the role of athermal nuclei in a polyethylene solution above its equilibrium dissolution temperature is played by stable associates, which we previously detected in other systems by means of direct electron-microscopic methods for studying the structure of polymer solutions (1,2). It should be noted that, as in the case of the concentration dependence studied earlier, the appearance of structures in solutions depends sharply on the temperature of the solution and occurs above the equilibrium dissolution temperature.

Fig. 4. Dependence of the induction period τ on the crystallization tempera-

Figure 4: Dependence of the induction period τ on the crystallization temperature T_{cr}, on the dissolution time t, and on the dissolution temperature.

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Received
22 V 1965

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